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Macroporous Carbon Supported Zerovalent Iron for Remediation of Trichloroethylene

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ABSTRACT: Groundwater contamination with chlorinated hydrocarbons has become a widespread problem that threatens water quality and human health. Permeable reactive barriers (PRBs), which employ zerovalent iron, are effective for remediation; however, a need exists to reduce the economic and environmental costs associated with constructing PRBs. We present a method to produce zerovalent iron supported on macroporous carbon using only lignin and magnetite. Biochar-ZVI (BC-ZVI) produced by this method exhibits a broad pore size distribution with micrometer sized ZVI phases dispersed throughout a carbon matrix. X-ray diffraction revealed that pyrolysis at 900 °C of a 50/50 lignin−magnetite mixture resulted in almost complete reduction of magnetite to ZVI and that compression molding promotes iron reduction in pyrolysis due to mixing of starting materials. High temperature pyrolysis of lignin yields some graphite in BC-ZVI due to reduction of carbonaceous gases on iron oxides. TCE was removed from water as it passed through a column packed with BC-ZVI at flow rates representative of average and high groundwater flow. One-dimensional convection−dispersion modeling revealed that adsorption by biochar influences TCE transport and that BC-ZVI facilitated removal of TCE from contaminated water by both adsorption and degradation.

KEYWORDS: Trichloroethylene, Biochar, Zerovalent iron, Macroporous carbon, Permeable reactive barrier

INTRODUCTION

Permeable reactive barriers (PRBs) have been widely used to remediate groundwater contaminated with chlorinated hydrocarbons.1,2 Zerovalent iron (ZVI) is most commonly employed in PRBs as an electron source to reductively dechlorinate the parent molecule to residual hydrocarbon and chloride. Although effective, PRBs are costly because of expensive raw materials. Poor adsorption affinity and low contaminant solution concentrations limit the kinetics of remediation, particularly affecting performance during high groundwater velocities. Expected service lives of PRBs was originally estimated at around 25 years; however, a recent lifecycle analysis reported that most PRBs only operate for about 10 years. This is due to declining reactivity of the permeable barrier material and declining hydraulic conductivity due to illuvial deposition of soil materials.1 These challenges call for a need to improve reactive barrier material to increase reliability and service life. Improved PRB material and construction methods would have positive impacts on the economics and performance of this technology. Further, alternate PRB media with lower global warming impact would more comprehensively benefit the environment than material produced by conventional means.3 Ideally, new technologies designed to produce PRB media with improved reliability and performance characteristics should also employ production practices that consume less energy and emit less greenhouse gases than current manufacturing processes.

Various approaches to improving reaction kinetics of PRB media have recently been reported: comixing activated carbon (AC) with ZVI,4−7 catalyst enhanced ZVI such as palladized ZVI,5−7 and development of biochar-ZVI (BC-ZVI)6−10 and AC-ZVI composites.11 Both BC-ZVI and AC-ZVI composites demonstrate increased degradation kinetics of TCE over ZVI, due to adsorption of the contaminant on the C phase. Despite

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promising performance reports, the high costs of activated carbon, binding agents, and rare-earth metals render options that employ these materials cost-prohibitive. Furthermore, leaching of certain catalyst metals poses other environmental risks; adding to the incumbent problem of the contaminant. All of these approaches lead to materials designed to be mixed with sand, as PRBs have been traditionally constructed, offering no solution to prevent pore clogging and decreasing hydraulic conductivity caused by soil illuviation. Production of reactive media reported in most of these studies employed borohydride reduction that is also costly,12 energy-intensive, and offers no way to reduce the climate impact of ZVI production.13

Pyrolysis of biomass pretreated with iron salts has been demonstrated to produce ZVI.8,10,14 In pyrolysis, organic materials are heated under low-oxygen conditions, thermally transforming the organic material into charcoal, also known as biochar, while oxidized iron is simultaneously reduced to ZVI and other crystalline forms of iron. Biochar production can be C neutral as the amount of atmospheric C sequestered in soil may equate to C released from fossil fuel utilized for harvesting and processing of biomass.15,16 The carbon sequestered in soil with biochar application and replacement of fossil fuel with biorenewable C to produce ZVI both reduce carbon dioxide and ZVI, respectively; however, feedstock chemistry and pyrolysis temperature in ZVI, respectively, feedstock chemistry and pyrolysis temperature influenced the reduction of iron.14 Pyrolysis based production of ZVI is potentially beneficial to the environment and more cost-effective than current production methods as biorenewable organic materials and low-cost iron oxides can be used for feedstocks.

Permeable reactive barriers require hydraulic conductivities greater than that of surrounding soil in order to perform. Pyrolysis-based ZVIs previously reported4,10,14 were small particulates that would be subject to eluviation and displacement in a PRB. One way to overcome possibly this challenge is to produce large particle BC-ZVI for use as media in PRBs. This innovation would eliminate the need for sand matrices in PRB construction. Biochars produced from most biomass feedstocks resemble precursor materials by size and shape characteristics. Even the anatomical structure of plant materials is preserved.17 Frangibility and low crushing strength of charcoals and biochar contribute to rapid physical deterioration in production and handling, thus even sizing of feedstock could only produce an ideal biochar size fraction of limited yield. For this reason, granular activated carbons cost several times more than powders. Producing large particle size biochar is thus challenging and processes that utilize whole plant materials could at best be optimized with low yield to produce large particle BC-ZVI.

We sought to address the need for low-cost but effective PRB media with a minor climate impact, by producing biochars from mixtures of lignin and magnetite. Lignin is an abundant and low-cost plant biopolymer that is available as a byproduct from paper pulp processing, sugarcane processing, and second generation ethanol production; lignin is biorenewable, and is often burned for process heat or landfilled. We previously employed ferric chloride to produce BC-ZVI; however, we found that significant chloride is volatilized in high temperature pyrolysis, potentially creating a hazard in the pyrolysis effluent.14 Magnetite (Fe₃O₄) is abundantly available as an iron ore, can be obtained at low-cost in bulk quantities in a powdered form, and reduces problematic discharge of noxious gases in pyrolysis effluent. We hypothesized that pyrolysis of mixtures of lignin and powdered magnetite would yield BC-ZVI materials that possess appropriate physical and chemical properties for PRB use.

**Materials and Methods**

**Biochar Preparation.** The conditions used in biochar preparation were learned in our earlier research, specifically, pyrolysis temperature, heating time, and selection of a low-ash biomass feedstock. Biochars were prepared by slow pyrolysis of lignin (control biochar) or lignin–magnetite mixtures in a stainless steel box contained in a muffle furnace and heated from ambient temperature to 900 °C over 4 h. During pyrolysis and throughout cool-down, samples were purged under 200 mL min⁻¹ N2 gas. Lignin was supplied by Archer Daniels Midland Corporation. This lignin was a coproduct of their Acetosolv process, a modified organosolv process, which is used to extract cellulose from corn stover for fuel-ethanol production. Magnetite was ore grade powder obtained from the Division of Lands & Minerals, Minnesota Department of Natural Resources and was dried in a convection oven prior to use. Lignin was ground in a mortar and pestle. Lignin and magnetite mixtures of 50/50 or 30/70 gravimetric ratios were mixed in a beaker and immediately pyrolyzed (unpressed sample). Pressed samples were prepared by compression molding of lignin–magnetite mixtures in a 4 in. 1D cylindrical aluminum compression mold preheated to 180 °C under 20 ton pressure (about 239 MPa), after which the resulting pellet was pyrolyzed (pressed samples). As pyrolysis yielded large intact solid loaves, resulting biochars were diced on a cutting board and screened between #4 and #12 screens (1.68 to 4.76 mm). This granule fraction was utilized for all analyses. Samples were stored in plastic bags after production.

**X-ray Diffraction (XRD) Analysis.** Diffraction patterns of biochar samples were collected from 10 to 90° 2θ with a Siemens D5000 X-ray diffractometer using Cu Kα radiation generated at 40 kV and 30 mA in step scan mode with a step size of 0.05° 2θ and a dwell time of 7 s per step. Fixed 1.0° divergence and 3.0° antiscattering slits were used with a scintillation counter. Random powder mounts of biochars ground in an agate mortar were analyzed at ambient temperature and humidity. The XRD patterns were analyzed using JADE v9.0.

**Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDS) Analysis.** Microscopy was performed with a FEI QUANTA FEG 250 scanning electron microscope using a 10 kV beam of about 1 nA. Images were collected using secondary electrons. Elemental maps were obtained by energy dispersive X-ray analysis using an Oxford Aztec EDS. Granular samples were mounted to the top of a 12.5 mm carbon stub using double-sided graphite tape by compressing the taped stub against a subsample of biochar. For elemental analysis, 1 g samples of biochar were ground in an agate mortar, transferred to a sample cup, and dosed with several drops of hexane which was used to extract adhesive from tape. The adhesive was necessary to hold biochar particles in place to avoid microscope contamination. With volatilization of hexane, the small amount of C added to the samples by the adhesive likely did not alter the bulk sample composition. Elemental analysis was performed by averaging triplicate EDS spot analyses. Thermal combustion analysis using an Elementar Vario Micro Cube was also performed to determine more accurately C, H, N, and S contents.

**Raman Spectroscopy.** Raman measurements were performed at ambient temperature using an XploRa Plus confocal Raman microscope (Horiba Scientific/FY, France) equipped with a 532 nm laser excitation source, operated at 25 mW. An objective with a 0.9 numerical aperture (Olympus, Melville, NY) was used to collect the Raman signal. Biochars were ground in a ball mill for 2 min to a fine powder. Graphite standards (UCAR SP-1, Graphite Standard I, Lot# B74, Union Carbide; Sigma-Aldrich synthetic graphite, Graphite Standard II, Lot# 08017EH) were analyzed as received. Approximately
20 mg of sample was pressed onto a glass slide forming a dense layer about 1 mm thick, and placed on the microscope sample holder for analysis. This was repeated 6 times for each sample. Reported spectra were averaged from 6 subsamples acquired in triplicate, for a total of 18 spectra, with a 10 s acquisition time for each spectrum.

Miscible-Displacement Experiment. Breakthrough curves of aqueous TCE were measured using stainless steel 22 mm ID × 100 mm columns (Alltech) packed with biochar granules using a modified influent pulse method described by Casey et al. (2000). The pressed 50/50 BC-ZVI and the biochar control materials were used for this study. Because BC-ZVI was 3 months old when breakthrough curve measurements were performed, ZVI was assessed prior to analysis using XRD in which the (110) reflection of ZVI was measured and intensities of 3 months old to fresh were compared. Two flow rates were employed, representative of high (12.2 mm min\(^{-1}\)) and average (5.6 mm min\(^{-1}\)) groundwater pore water velocities. These flow rates are reported as "fast" and "slow" in the results. Milli-Q water was used for preparation of TCE (>99% Alfa-Aesar, Lot # X17A014) solutions and breakthrough curve measurements. Water was delivered by peristaltic pump and one-pore volume of pulses ~50 mg L\(^{-1}\) TCE were injected by a programmable syringe pump equipped with a stainless steel syringe (Cole Parmer). Assay of pulse samples taken prior to and after pulse was averaged to determine influent TCE concentration. Both pumps were calibrated to deliver equal flow rates. Columns were initially purged with drops of 50% HCl, vials containing about 35 mL of water, 250 mg of ascorbic acid, and six stainless steel tubing and sequential samples were collected in 1.2 mL pycnometry and bulk density was determined from the mass of biochar measurements. Particle density of biochars was measured by helium pycnometry and bulk density was determined from the mass of biochar contained in the columns. Column effluent was passed through stainless steel tubing and sequential samples were collected in 1.2 mL gas chromatography (GC) sample vials and immediately sealed without headspace using vial caps equipped with Teflon seals. Aliquots were withdrawn from these sample vials and diluted into 40 mL glass vials containing about 35 mL of water, 250 mg of ascorbic acid, and six drops of 50% HCl, filled with water to eliminate headspace, and capped with plastic caps equipped with pierceable Teflon septa. TCE and degradation byproducts were assayed in accordance with EPA Method 524.2 using a purge and trap GC (Varian CP 3800) equipped with a Tekmar Dorhmann 25 mL purge vessel, Varian Saturn 2200 mass spectrometer, and Restek RTX VMS 60 m × 0.32, 0.32 mm ID GC column. Restek 502 Cal 200 Mega Mix, 502 Calibration Mix 1, and S24 Internal Standard Surrogate Mix were used for calibration. Data were processed using a Saturn GC/MS workstation v5.52.

Mathematical Model. A convection–dispersion chemical transport model was fitted to the measured column effluent breakthrough curve data. CXTFIT v2.1 was used to estimate the retardation factor (R) and combined first-order adsorption/degradation rate coefficient (μ). In this model, R implies the empirical distribution of TCE between the adsorbed and liquid phases. Because BC-ZVI adsorbs and actively degrades TCE, an empirically regressed coefficient μ is chosen to represent the efficiency of TCE reduction in comparing BC-ZVI to control biochar. Therefore, the measured TCE breakthrough curves at two flow rates for BC-ZVI and control were fitted with the convection–dispersion equation (CDE) for one-dimensional transport of TCE, subject to equilibrium adsorption and first-order degradation kinetics:

\[
R \frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial z^2} - v \frac{\partial c_i}{\partial z} - \mu c_i
\] (1)

where \(c_i\) is the resident concentration of TCE, \(v\) is the average pore-water velocity, \(t\) is time, \(z\) is distance from the influent end of the column, and \(D\) is the dispersion coefficient, which relates to the dispersivity (λ) and \(v\), i.e., \(D = \lambda v\). \(R\) is given by

\[
R = 1 + \frac{\rho_b K_d \mu}{\theta}
\] (2)

and \(\mu\) is given by the first-order rate in the liquid, \(\mu_b\) and adsorbed phases, \(\mu_a\).

\[
\mu = \mu_i + \frac{\rho_b K_d \mu_i}{\theta}
\] (3)

\(\rho_b\) is the bulk density of the packed biochar granules, \(K_d\) is the distribution coefficient, and \(\theta\) is the volumetric water content. A nonlinear least-squares optimization method\(^{14}\) is used in CXTFIT to determine the optimal values of \(R\) and \(\mu\). In this model, the values of \(\lambda\) were determined from the fast breakthrough curves and applied to fit the slow breakthrough curves for respective control and BC-ZVI treatments.

RESULTS AND DISCUSSION

Biochar Characterization. Lignin and magnetite employed in this study were fairly clean raw materials, with the lignin having an ash content of 0.43% and overnight loss on drying at 105 °C and XRD analysis (not shown) of the magnetite revealed 7% moisture content and evidence of both magnetite and maghemite, though maghemite was the dominant crystalline structure detected in the sample. Elemental analysis of the resulting BC-ZVI and control biochar (pyrolyzed lignin without magnetite) presented in Table 1 reveal that the control biochar was well carbonized with approximately 8% O content, measured by the difference of N, C, H, S, and ash fractions determined by thermal combustion from unity, which is in good agreement with 10.47% O determined by SEM-EDS analysis. The low H content of this biochar is consistent with extensive condensed aromatic character of C.\(^{22}\) Though the 30/70 lignin–magnetite mixtures were prepared and pyrolyzed under the same conditions, lower C yield is observed in BC-ZVI produced from unpressed materials, suggesting that compression molding causes higher char yield. More production replicates would be necessary to understand better the effect of compression molding on C yield. The N, C, H, and S contents determined by thermal combustion are more verifiable than determined by SEM-EDS analysis, because of better representative sampling and the fact that particle settling in the sample cup used in the EDS analysis can cause bias as lighter particles can redistribute to the top of the sample during preparation. The major elements detected in these biochars by EDS are C, O, and K likely as K\(_2\)O due to the lack of other anions, and additionally Fe for BC-ZVI.

Scanning electron microscopy revealed a broad pore size distribution in both control biochar and BC-ZVI ranging from micrometers to several millimeters (Figure 1). Large pores
promote hydraulic conductivity and are necessary for PRBs to function effectively. Some pores observed in BC-ZVI may be continuous and allow for intraparticle transport, but inter-particle pore size can be designed by particle sizing. Thus, BC-ZVI production using lignin and magnetite could be employed to create any size fraction or desired shape of the product material. Elemental analyses presented in Table 1 reveal that C, Fe, and O predominantly constitute BC-ZVI. Lighter regions in the 5000× micrographs of BC-ZVI correspond to metal phases as reflecting more electrons back to the detector due to large differences in atomic mass between any possible metals and carbon. As the only metal dominating is iron, Fe (56.45) reflects more electrons back to the detector. These iron phases ranged from nanometers to several micrometers in size. No differences were observed in the distribution or size of Fe phases in BC-ZVI produced from different feedstock ratios. Iron phases in BC-ZVI were separated by regions of C, suspended by the solid foam matrix of biochar C. This physical structure was owed to the physical properties of the particular lignin selected for this study that flowed under pressure. Gas expansion during pyrolysis expanded lignin as it pyrolyzed, resulting in a solid porous foam. We evaluated several sources of lignin for this study; however, only the ADM lignin yielded the desired physical structure of BC-ZVI upon pyrolysis; water-soluble lignins yielded powder biochars (unreported data from this study). The lignin employed to produce biochars for this study was water and hexane insoluble material of frangible nugget consistency that exhibited decreased viscosity upon heating. Plasticity of lignin was crucial to successful melt processing as the lignin was used to suspend magnetite particles in a thermoplastic matrix that transformed to char and gases upon pyrolysis.

XRD patterns of BC-ZVI and control biochar produced from lignin are depicted in Figure 2. The d-spacings and relative intensities for XRD peaks of mineral phases detected in the biochars are provided in Table 2 to facilitate interpretation of the diffraction patterns. Thermal transformation of lignin and magnetite mixtures heated to 900 °C yielded biochar composites with ZVI and residual magnetite and wüstite. Silicon in lignin transformed to quartz with pyrolysis. Evidence for wüstite was observed in XRD patterns of biochars prepared from the 30/70 lignin–magnetite mixtures. The relative intensity of wüstite to α-Fe (ZVI) and magnetite peaks was greater for BC-ZVI produced from the pressed versus the unpressed mixture. Phase transformation of magnetite to ZVI during pyrolysis was a reduction process that proceeded through an intermediate wüstite phase at high temperature and low oxygen fugacity. Wüstite was a metastable phase that eventually decomposed to ZVI and magnetite after cooling. Greater relative intensities of wüstite reflections observed in the XRD pattern of 30/70 pressed biochar indicated that more Fe was in this phase after pyrolysis, illustrating an effect of
Reduction by solid C10 and reducing gases produced at high temperatures resulted in a greater reduction of Fe observed in the 50/50 mixture. This greater reduction is attributed to the 50/50 mixture yielding the most reduction of Fe to zerovalent iron (ZVI). This greater reduction is most likely due to the transformation of magnetite to ZVI in this mixture. Although the control BC-ZVI produced from the 50/50 mixture exhibited higher intensities of the G band, with greater relative intensities of the ZVI band, the wustite band was observed in all BC-ZVI samples. The 50/50 mixture exhibited greater intensities of the ZVI band, with greater intensity observed in the BC-ZVI material. The 50/50 mixture displayed greater intensities of the wustite band, with greater intensity observed in the BC-ZVI material.

Figure 2. XRD patterns of BC-ZVI produced from lignin and magnetite and control biochar produced from lignin. Letter identifiers describe feedstock preparation: a = 50% lignin/50% magnetite (pressed), b = 30% lignin/70% magnetite (pressed), c = control biochar from lignin, d = 30% lignin/70% magnetite (unpressed). Peak labels represent crystalline structures found in biochar: α-Fe = Zerovalent iron, G = graphite, M = magnetite, Q = quartz, W = wustite.

The control biochar (c) exhibited a diffraction pattern typical of biochar, with broad amorphous carbon reflections centered at 22°, 44°, and 80° 2θ. Although C in these biochars was dominantly amorphous, evidence for graphite was observed in BC-ZVI, with greater intensity observed in the BC-ZVI material. The control biochar was likely caused by better crystalline ordering of C that was observed in the BC-ZVI material.

Table 2. d-Spacing (d) and Relative Intensity (I) for XRD Peaks of Mineral Phases Found in the Biochars (JADE v9.0)

<table>
<thead>
<tr>
<th>dθ (°)</th>
<th>d(Å)</th>
<th>I(int)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.506</td>
<td>3.36</td>
<td>100</td>
</tr>
<tr>
<td>44.6</td>
<td>2.03</td>
<td>50</td>
</tr>
<tr>
<td>54.652</td>
<td>1.678</td>
<td>80</td>
</tr>
<tr>
<td>77.4</td>
<td>1.232</td>
<td>30</td>
</tr>
<tr>
<td>83.394</td>
<td>1.158</td>
<td>50</td>
</tr>
<tr>
<td>86.907</td>
<td>1.12</td>
<td>20</td>
</tr>
<tr>
<td>101.6</td>
<td>0.994</td>
<td>40</td>
</tr>
</tbody>
</table>

Graphite | Quartz | Magnetite | ZVI (α-Fe) | Wustite |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (°)</td>
<td>d(Å)</td>
<td>I(int)</td>
<td>2θ (°)</td>
<td>d(Å)</td>
</tr>
<tr>
<td>20.86</td>
<td>4.255</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.423</td>
<td>2.532</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>43.059</td>
<td>2.099</td>
<td>20</td>
<td></td>
<td></td>
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<tr>
<td>53.379</td>
<td>1.715</td>
<td>10</td>
<td></td>
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<tr>
<td>56.936</td>
<td>1.616</td>
<td>30</td>
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<tr>
<td>62.539</td>
<td>1.484</td>
<td>40</td>
<td></td>
<td></td>
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<tr>
<td>73.929</td>
<td>1.281</td>
<td>10</td>
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</tbody>
</table>

Table 3. Raman Shifts of D and G Bands of Graphite Standards, Lignin Control Biochar, and BC-ZVI

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Band (cm⁻¹)</th>
<th>G Band (cm⁻¹)</th>
<th>D/G Height Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Standard I</td>
<td>1335</td>
<td>1562</td>
<td>0.013 ± 0.002</td>
</tr>
<tr>
<td>Graphite Standard II</td>
<td>1326</td>
<td>1554</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>Lignin Control Biochar</td>
<td>1330</td>
<td>1573</td>
<td>1.18 ± 0.02</td>
</tr>
<tr>
<td>Unpressed 30/70 BC-ZVI</td>
<td>1321</td>
<td>1566</td>
<td>1.29 ± 0.03</td>
</tr>
<tr>
<td>Pressed 50/50 BC-ZVI</td>
<td>1324</td>
<td>1563</td>
<td>1.28 ± 0.03</td>
</tr>
<tr>
<td>Pressed 30/70 BC-ZVI</td>
<td>1324</td>
<td>1568</td>
<td>1.21 ± 0.02</td>
</tr>
</tbody>
</table>

D/G Height ratio reported as mean ± standard deviation.

Raman spectroscopy was performed on biochars to obtain information regarding the structure of carbon in these materials. All data were processed using Igor Pro 6.37 scientific analysis and graphing software (Wavemetrics, Lake Oswego, OR). Spectra were fitted to a Gaussian function with a linear baseline using the multfit peak function in order to extract peak intensity (height) and center position (Table 3). Graphitic material exhibits characteristic Raman bands around 1580 cm⁻¹ (E₂g, G band) and 1360 cm⁻¹ (A₁g, D band). The D band is attributed to the presence of structural defects. The intensity ratio I_D/I_G between the D and G band has been widely used as a measure of defects in graphite-based materials. The D band and G band are present in the Raman spectra of the biochar materials, illustrating the graphitic character of the samples. However, the biochar samples present broader G and D bands compared to the highly ordered graphite standards, which indicates a highly disordered structure in the biochar samples. The I_D/I_G intensity ratios provided in Table 3 also reveal a highly disordered graphitic character of C in the BC-ZVI and control biochar, with the graphite standards exhibiting one to 2 orders of magnitude lower I_D/I_G ratios compared to the spectra of biochars. I_D/I_G ratios in BC-ZVI at different lignin/magnetite ratios are statistically greater (p ≤ 0.0266) than the lignin control biochar, suggesting that the presence of magnetite during the pyrolysis of lignin induces some level of disorder within the biochar structure, giving C in BC-ZVI samples a greater level of disorder that detected in control biochar.

Graphitic reflections observed in the XRD patterns of BC-ZVI (Figure 2) indicate crystalline character of graphite in BC-ZVI. This difference between graphitic C in BC-ZVI and the control was likely caused by better crystalline ordering of C that

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Figure 3. Raman spectra of graphite standards, lignin control biochar, and BC-ZVI.

Figure 4. TCE Breakthrough curves of control and BC-ZVI and model parameters.

Figure 4. TCE Breakthrough curves of control and BC-ZVI and model parameters.

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portation. Large (3 mm) intraparticle pore diameters observed in BC-ZVI produced in this study and the fact that BC-ZVI could potentially be sized in production indicate that BC-ZVI could be designed to exhibit greater saturated hydraulic conductivities than sand-ZVI mixes, thus would be resistant to soil deposition within the PRB, extending service life, and eliminating the need for a sand matrix. For these reasons, column experiments were performed using only packed granules to reveal how BC-ZVI without sand would perform as a PRB. Further research is needed to assess this BC-ZVI as a PRB to understand three-dimensional spacial and time dependent transport of chlorinated hydrocarbon contaminants and to evaluate service life of PRB constructed entirely of BC-ZVI.

Cost Implications. BC-ZVI offers advantages over ZVI in that contaminant adsorption increases local contaminant concentration near the reactive surface. AC-ZVI would perform similarly if not better; however, it comes at much higher cost as AC is inherently expensive, with PAC starting at around $750/ton and GAC exceeding $2000/ton. NZVI exhibits rapid dechlorination; however, production is costly due to the cost and environmental impacts associated with production of borohydride, and BC-ZVI is used to reduce aqueous Fe$^{2+}$ to NZVI. NZVI can be introduced to contaminated soil as a colloid and has a short service life. This approach can be effective for rapid mitigation of contaminant plumes, but it is not viable for long-term in situ remediation. ZVI is probably the lowest cost in situ remediation technique for rapid removal of various contaminants from aqueous solutions. However, it is also expensive, starting at $500/ton for ironfilings and exceeding $1500/ton for micrometer size fractions. BC-ZVI can be produced from low-cost iron sources and biorenewable waste materials, offering a low-cost alternative to producing ZVI for water remediation, sequesters some atmospheric carbon as charcoal, and lowers the environmental impact of current ZVI production.

CONCLUSIONS

Macroporous lignin supported ZVI was successfully produced by pyrolysis of lignin and magnetite at 900 °C. A 50/50 mixture of these materials yielded almost complete reduction of nanoparticle magnetite to ZVI. Compression molding promoted iron reduction due to mixing of feedstock materials achieved with melt processing. Residual magnetite and wüstite in fresh BC-ZVI suggested that longer pyrolysis times and greater lignin ratio could optimize production. Pyrolysis of lignin yielded carbon in control biochar and BC-ZVI that was both amorphous aren C and disordered graphite. Pulse breakthrough curves revealed that adsorption and degradation of TCE both influenced transport of this contaminant and that BC-ZVI produced from lignin and magnetite successfully degraded TCE. The production of BC-ZVI from lignin and magnetite would be very effective both in terms of cost and environmental impact. Further testing of space and time scales should be performed to evaluate use of this BC-ZVI as a PRB.

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Notes

The authors declare no competing financial interest.


